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Electron spin resonance and nuclear magnetic resonance of sodium macrostructures in strongly irradiated NaCl–K crystals: Manifestation of quasi-one-dimensional behavior of electrons

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Data from an investigation of electron spin resonance and nuclear magnetic resonance of NaCl–K (~1 mole%) crystals strongly irradiated with electrons imply the observation of a metal-insulator transition with decreasing temperature and the manifestation of quasi-one-dimensional electron motion in sodium macrostructures. © *1998 American Institute of Physics.* [S0021-3640(98)00403-4]

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Quasi-one-dimensional inorganic conductors with a complicated crystal structure and unusual properties—Peierls instability, the formation of a charge density wave (CDW) at low temperatures, nonlinear and anisotropic behavior of the conductivity, and so on—are of great interest. The properties of conductors with a CDW have still not been adequately studied, especially at low temperatures.[1] The complexity of the questions and the need to clarify them on more perfect crystals are a constant stimulus for both expanding the range of structures investigated and searching for and obtaining new one-dimensional compounds. Evidently, the suggestion[2] that conducting channels consisting of a quasi-one-dimensional alkali metal can form in simple NaCl-type structures under irradiation with high-energy electrons merits attention. The objective of the present work is to clarify this question experimentally. The methods of investigation consisted of electron spin resonance (ESR) and nuclear magnetic resonance (NMR), which can be used to identify reliably the nature of micro- and macrodefects in irradiated structures.[3]

The ESR and NMR experiments were performed on $3\times3\times1$ mm single-crystal samples of NaCl–KCl (1 mole %). The samples were irradiated in a linear accelerator with electron energy ~3.5 MeV. The total absorbed dose on the sample reached 150 Grad; the irradiation temperature was equal to 100–110 °C. The ESR and NMR signals were measured at 9.4 GHz and 10–105 MHz, respectively, and their behavior was studied in the temperature interval 8–450 K. The magnetic spin susceptibility, which is

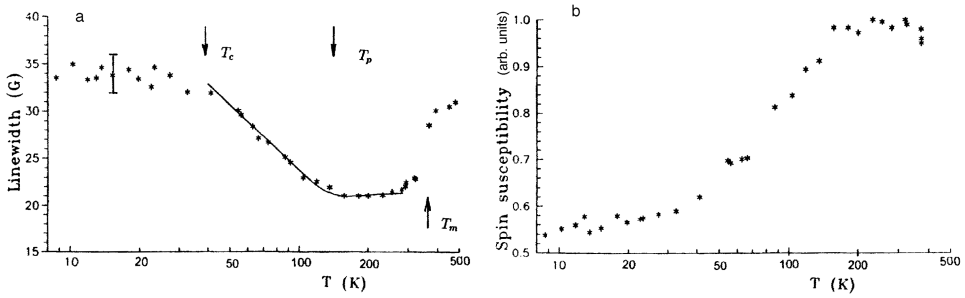

FIG. 1. Temperature dependences of the ESR linewidth (a) and spin susceptibility (b) in an irradiated NaCl–K crystal. The solid line was calculated from Eq. (1).

proportional to the total intensity of the ESR line, was investigated at the same time.

The temperature dependences of the ESR linewidth δH and spin susceptibility χ in irradiated NaCl–K are shown in Fig. 1. The temperature dependence of the intensity I of the NMR signal from metallic ^{23}Na nuclei in the same sample is displayed in Fig. 2 (here, for convenience in describing the data, the characteristic temperature ranges are distinguished from one another by the arrows). At temperatures above $T_p \sim 160$ K the behavior of the entire series of measured parameters was typical for metallic sodium. Here a nearly Lorentzian symmetric shape of the ESR line and a deviation of the g factor of the signal $\Delta g = g - g_0 = (-9 \pm 2) \times 10^{-4}$ from its value for a free electron ($g_0 = 2.0023$) were observed. One can see from Fig. 1 that the temperature dependence $\delta H(T)$ is linear with slope $\sim 2 \times 10^{-2}$ G·K^{-1}, and δH increases by ~ 5.5 G at the point $T_m \approx 370$ K, which is close to the melting point of sodium. The susceptibility χ of the sample behaves similarly to the Pauli susceptibility of the conduction electrons. Two NMR lines from ^{23}Na nuclei were observed: a wide line, corresponding to the nuclei of the ionic lattice of NaCl (and therefore of no interest), and a narrow line, arising at a higher frequency as a result of the presence of mobile electrons and corresponding to the nuclei of metallic sodium. This line is characterized by the standard temperature behavior for nuclei (the intensity is inversely proportional to temperature, Fig. 2), a small width ~ 0.5 kHz, and a Knight shift $K(300\ \text{K}) = 0.108\%$, which was almost temperature-independent. The data obtained (except for the values of δH) are in good agreement with the corresponding published data

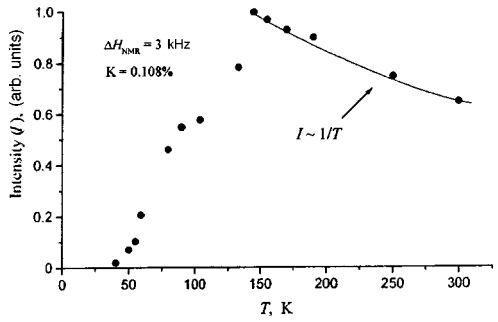

FIG. 2. Temperature dependence of the intensity of the NMR signal from metallic sodium nuclei in NaCl–K.

for sodium (see, for example, Refs. 3 and 4); this confirms the formation of a metallic phase in the sample. The measured value $\delta H(300\ \mathrm{K}) = 22 \pm 2$ G is approximately three times greater than the electron-phonon linewidth in bulk sodium (~ 6 G);[4] this could be a consequence of the additional effective interaction of electrons in the system.

A continuous transition to the properties of the insulator was observed with decreasing temperature. The form of the ESR signal changed, and below the point $T_c \sim 40$ K the signal consisted of a superposition of Lorentzian lines, indicating the appearance of a small variance in the g factors in the system. We were able to measure in the interval 8–30 K the shift of the ESR signal from its position at high temperatures. The shift was equal to $\Delta g = (-12 \pm 3) \times 10^{-4}$. One can see from Fig. 1 that δH increases with decreasing temperature and reaches the value 34 ± 2 G, while χ behaves unusually—it decreases and approaches the value $\chi(300\ \mathrm{K})/2$ (below T_c a ''plateau'' can be seen in both dependences). Near $T_p \sim 160$ K the NMR linewidth increased to ~ 3 kHz and below this temperature it remained constant, while the intensity $I(T)$ decreased continuously to zero. No signal was observed in the interval 8–38 K (Fig. 2).

The observed effects—the vanishing of the NMR signal near T_c and the vanishing of the magnetization $\chi_e(T)$ of the conduction electrons in the system—are a direct consequence of electron localization, which occurs in the region from T_p to T_c. The ''metallic'' ESR and NMR signals are not detected below T_c—a dielectric state of the system arises, and the ESR line observed in the dielectric phase is apparently due to some other (nonconducting) electrons, which contribute a fraction equal to approximately $\chi/2$ to the magnetization. In our view, on the basis of the following considerations, such electrons are F-center electrons. The irradiated alkali-halide crystals comprise systems with paramagnetic defects that can be controlled well. The main defects in strongly irradiated NaCl–K are exchange-coupled F centers (clusters), and when the new phase[b)]—sodium macrostructures (particles or, most likely, chains of the metal)—appears, these centers become the main type of defect in the metal lattice. ESR signals with close values of the g factors are observed from F centers and the metal. It seems to us unlikely that signals from other electronic states appear in the ESR spectrum. In the course of irradiation the electron density and, correspondingly, the intensity of the ESR line from conduction electrons grow and the form of the spectrum changes.[5,6] When the exchange interaction between F-centers becomes strong, which happens when the distance between the centers decreases values of the order of 2–3 lattice constants, the resonance line of the F centers narrows to 30–35 G; the shape of the line looks like a superposition of lines from different clusters of F centers and its integrated intensity (susceptibility) is almost temperature-independent. The interaction with conduction electrons leads to an even greater narrowing of the line from F centers, and the rapid diffusion motion of the conduction electrons averages the g-factor distribution existing in the system. As a result, narrow lines from F-center and conduction electrons become indistinguishable, and at high temperatures a combined resonance of both electronic systems can occur. Since a metal-insulator transition occurs in the system with decreasing temperature, a resonance line characterized by ESR parameters of only F centers will correspond to the dielectric phase, as was conjectured above.

An interesting result was obtained in the ESR measurements: As the temperature decreases, the linewidth δH of the resonance line at $T_p \sim 160$ K starts to increase in inverse proportion to χ (Fig. 1). This fact can shed light on the characteristic features of

the metal-insulator transition in the system and makes it possible to describe the observed behavior of $\delta H(T)$. Let us return to our conjecture that conduction-electron spins (which we denote by the index e) and the localized spins of F-center electrons (s) are both present in NaCl–K on the metallic side of the transition. In the presence of two spin subsystems, a sharp ''bottleneck'' regime (combined e and s electron resonances) is realized in NaCl–K, since the g factors of both systems are equal, $g_e = g_s$, and $1/T_{sL} > 1/T_{eL}$, where T_{sL} and T_{eL} are the spin-lattice relaxation times of the s and e electrons, respectively. A model of ESR of localized spins in a metal has been proposed in Ref. 7. In the case of a bottleneck the linewidth of the resonance line is $\delta H \approx (\chi_s T_{sL}^{-1} + \chi_e T_{eL}^{-1})/(\chi_s + \chi_e)$, i.e., the fraction of the magnetization for each subsystem is multiplied by the spin-lattice relaxation rate in this subsystem. As the temperature decreases, the susceptibility of the system $\chi = \chi_s + \chi_e$ decreases because χ_e decreases (by $\sim 50\%$) and in consequence χ_s—the contribution from localized spins—should be much greater than the Pauli susceptibility χ_e of the conduction electrons. Hence it follows that $\delta H \approx 1/T_{sL}$. Since the spin-lattice relaxation constant is controlled by the interaction with the conduction electrons, we have $1/T_{sL} \approx (1/2)\omega_{hf}^2 T_{se}$, where ω_{hf} is the hyperfine structure constant and T_{se} is the cross-relaxation time of F-center electrons to conduction electrons. From the balance equation $T_{se}/T_{es} = \chi_s/\chi_e$, where T_{es} is the cross-relaxation time of conduction electrons to F-center electrons, we arrive at the desired result[7]

$$\delta H \sim (\chi_s/\chi_e) T_{es}, \tag{1}$$

where χ_e decreases with temperature, χ_s is almost temperature-independent, and $1/T_{es} = 2\pi c \rho J^2$ (c is the localized-spin density, ρ is the density of states at the Fermi surface, and J is the exchange interaction constant of s and e electrons). The behavior of $\delta H(T)$ can be described in the present model of two types of electrons[7] with $\rho = 30\ \mathrm{eV}^{-1}$ (from the free-electron approximation), $J \approx 1.2 \times 10^{-5}$ eV, $\omega_{hf} = 9 \times 10^9\ \mathrm{s}^{-1}$, and density $c \cong 6 \times 10^{18}\ \mathrm{spin/cm}^3$, as found from the ESR measurements. To obtain agreement with experiment, a T-dependent ''intrinsic'' (electron-phonon) linewidth in sodium, which is ~ 6 G at 300 K,[8] must be added to expression (1).

It follows from Fig. 1a that the linewidth increases logarithmically with decreasing temperature, $\delta H \sim \ln(1/T)$. This behavior is confirmed by ESR measurements on samples with a high density of localized impurities (F-centers). Taking into account simultaneously this contribution and the phonon contribution to δH, which decreases with temperature, explains the presence of a minimum in the observed temperature dependence $\delta H(T)$. Figure 3 shows a minimum of the linewidth of the resonance line for three NaCl–K samples with different localized-spin densities. According to Refs. 4 and 8, the temperature-dependent part of the ESR linewidth in alkali metals varies as the temperature-dependent part of the resistivity. As a result, the behavior of the minimum of the linewidth (Fig. 3) is analogous to that of the minimum of the resistivity in dilute alloys with magnetic impurities (Kondo effect[c)]). Within the limits of the measurement accuracy of the electron density c, the temperature of the minimum $T_{\min}$ varies as $\sim c^{1/5}$ (see, for example, Ref. 9). Measurements of the ac conductivity at 400 Hz to 20 kHz in the same types of samples showed a sharp peak near $T_{\min}$ (see Ref. 2). Moreover, the appearance of a maximum in $\delta H(T)$ (instead of a ''plateau'') in some samples at low temperatures was likewise predicted by the theory of Ref. 9. The exchange interaction between conduction electrons and a local moment corresponds to a scattering process in which the spin of the conduction electron can flip and at the same time the orientation of

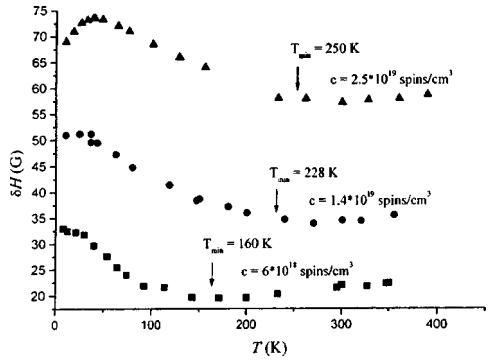

FIG. 3. Minimum of the ESR linewidth in NaCl–K samples with different density of localized impurities (F-centers). The position of the minimum depends on this density.

the impurity spin changes.[9,10] The latter fact could be used to explain the locations of conduction electron localization in the sample, but this requires that the contribution of localized impurities to the linewidth be taken into account in detail on the basis of an accurate model.

It follows from our data that electron localization occurs in NaCl–K and that metallic resonances die out in the transition region (40–160 K). This behavior is typical for quasi-one-dimensional systems and in many cases it is a consequence of a Peierls transition at temperature T_p, which usually lies in the range 100–200 K. Below this temperature lattice distortions arise, giving rise to a gap at the Fermi surface, a decrease of the electron energy, and electron localization. The largest changes in the system occur at temperature $\sim T_p/4$ (transition to a dielectric state, observation of superstructure—a CDW with period $2k_F$, and so on). The hypothesis that the transition in NaCl–K is of a Peierls character can be confirmed or rejected by means of x-ray observations of the superstructure at temperatures below 40 K.

The observation of a frequency dependence of the spin-lattice relaxation rate T_1^{-1} of the metallic nuclei provides a direct check of the quasi-one-dimensionality of the conduction electron motion. Such measurements have been performed on different organic conductors.[11] Figure 4 shows the frequency dependence of the relaxation rate T_1^{-1} of the metallic ^{23}Na nuclei in a NaCl–K crystal at room temperature. One can see that the relaxation rate varies as $T_1^{-1} \sim \nu_n^{-1/2} \sim \nu_e^{-1/2} \sim H_0^{-1/2}$ in magnetic fields 50 G$<H_0<$5 kG, where ν_e is the electronic Larmor frequency and ν_n is the nuclear Larmor frequency. The figure also shows a frequency-independent value of the nuclear relaxation rate in bulk sodium $T_1^{-1}=62.5\ \mathrm{s}^{-1}$ measured in high fields ($H_0 \gg 5$ kG). The diffusive behavior of electrons first appears at frequencies $\omega_e < \omega_c \approx (1/\tau)N$, where ω_e is the electronic frequency, $\tau \cong \lambda/\nu_F$, λ is the electron mean free path (350 Å at 300 K), ν_F is the Fermi velocity, and the parameter $N \cong (d/a)^2$ takes into account the geometry of the conductor (a is the lattice constant and d is the transverse size of a chain). In the case $\omega_e < \omega_c$, there is a high probability that an electron will repeatedly interact with the same nucleus in the time interval $2\pi/\omega_e$. In contrast to the three-dimensional case, this results in a frequency-dependent relaxation rate:[11]

$$(T_1T)^{-1} = C_{1g}(\omega_e) + C_2, \tag{2}$$

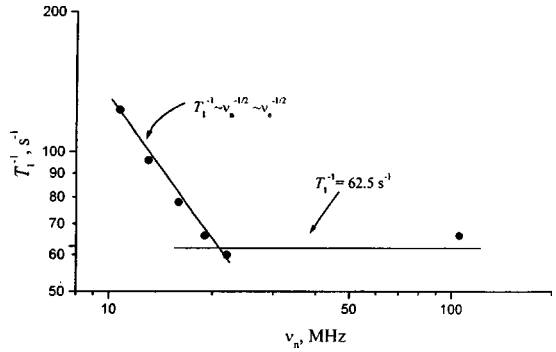

FIG. 4. Frequency dependence of the spin-lattice relaxation rate T_1^{-1} of metallic nuclei in a NaCl–K crystal at room temperature (ν_e(GHz)$=2.486\nu_n$(MHz)).

where

$$g(\omega_e)=\{[1+(1+k)^{1/2}]/2(1+k)\}^{1/2}, \quad k=\omega_e^2\tau_e^2,$$

τ_e is the characteristic electron lifetime on a given chain with a given direction of the spin, and the parameters C_1 and C_2 are independent of ω_e. It follows from Eq. (2) that in the case $k \gg 1$, when relaxation of the electronic spin and hopping between chains can be neglected, a square-root frequency dependence should be observed $g(\omega_e)=(1/\omega_e)^{1/2}$. It is obvious from Fig. 4 that for $\omega_e > \omega_c \approx 2\times 10^{11}$ s^{-1} the nuclear relaxation rate no longer depends on frequency, and the observed value $(T_1T)^{-1}=0.2$ (s·K)$^{-1}$ is close to the value for bulk sodium. Hence the average transverse size of the conducting channels can be estimated as $d \cong a(\nu_F/2\pi\lambda\nu_c)^{1/2} \cong 12a$, i.e., quasi-one-dimensional behavior of the electrons can appear at room temperatures.

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[b)]Nonequilibrium growth of an electronic structure consisting of F-centers and formation of a metallic lattice on the basis of such a structure occur at high irradiation temperatures and with the participation of impurities, such as K, OH^-, or F. A metallic phase does not arise in pure NaCl crystals.[5,6]

[c)]As is well known,[9,10] the expression for the interaction energy of an electron with impurity atoms contains a term $\mathbf{J}(\mathbf{s}\cdot\mathbf{S})$ (where $\mathbf{s}$ is the electron spin and $\mathbf{S}$ is the impurity spin), which in high orders of perturbation theory leads to a spin-dependent contribution to the electron scattering and therefore to the resistance. Kondo explained the growth in the resistance with decreasing temperature and the appearance of a minimum of the resistance whose position depends on the density of magnetic impurities.

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